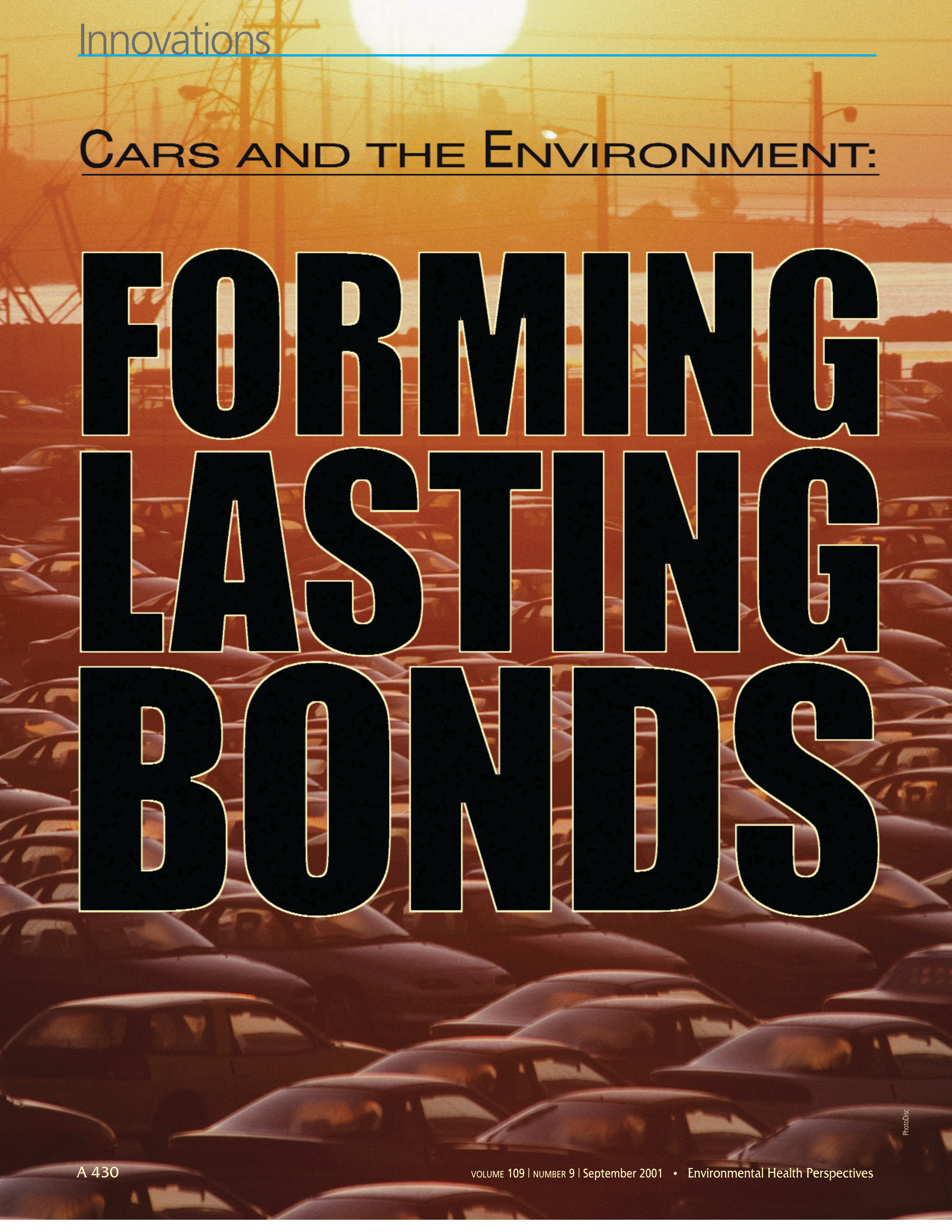
Cars and the Environment: Forming Lasting Bonds



PhotoDisc

Most anyone would agree that one of the most important aspects of people's love affairs with their automobiles is the color of the vehicle. Whether vibrant red, stately gray, or stealthy black, the color of a car says something about its driver (or at least, advertising has convinced us it does). So making the color last is an important consideration in automobile manufacturing. But color is not the only consideration. Equally if not more important is fuel efficiency and emissions ratings. Today, a new process that enables auto body parts made of lightweight and environmentally friendly polypropylene plastic to be permanently coated with paint—once an impossibility—may allow vehicle manufacturers to appeal to car buyers on both the aesthetic and economic levels.

Polypropylene is a marvelous substance. It's lightweight, it's durable, it's easy and inexpensive to manufacture, and it uses few environmentally damaging chemicals. For all these benefits, it does have its flaws. Due to its molecular makeup, the surface of polypropylene is all but impossible to paint or to bond with any other substance, making it difficult to use in some applications, including automobile manufacturing. Using a process that has been dubbed "SICOR" (for ***si***lane-on-***cor***ona), Voytek Gutowski, a researcher with Australia's federal science agency, the Commonwealth Scientific and Industrial Research Organisation (CSIRO), has been able to treat these types of polymers to create a surface that is both paintable and bondable.

The process was tested by Australian carmaker Holden (a division of General Motors) by attaching treated polypropylene body side moldings to a Holden vehicle, which was then durability-tested over 40,000 km on the test track at Lang Lang Proving Ground, 95 km southeast of Melbourne. In order to predict field performance, additional laboratory tests on identical parts were carried out through extremes of heat and humidity simulating environmental conditions likely to be encountered. At the end of the tests, according to Larry Little, chief of CSIRO Building, Construction, and Engineering, "it proved impossible to remove the moldings without damaging the door panels themselves. Other tests showed [SICOR] bonds automotive paint to molded polymer parts like bumper bars so strongly that the polymer itself will break before the paint can be pulled from the surface."

Chemical Velcro

Polypropylene is part of a chemical family known as the polyolefins. Polypropylene is formed of linked carbons, the first linked to two hydrogen atoms, the second to a hydrogen atom and a methyl group (CH_3). According to Gutowski, polyolefins are desirable engineering plastics for several reasons. "Polyolefins such as polypropylene can be made either very rigid or extremely flexible," he says. "They don't shatter easily, nor do they degrade easily with exposure to the elements, and they're easily processable.

The problem, says Gutowski, is that to paint or bond these plastics, their surfaces must first be modified, and the processes currently used to do that involve the use of solvents containing such environmentally hazardous substances as toluene and xylene. According to the Agency for Toxic Substances and Disease Registry, exposure to increasing levels of toluene can cause symptoms including hearing and color vision loss, nausea, depression of the central nervous system, reversible kidney damage, and death, while exposure to xylene can cause nausea, pulmonary edema, and death. Says Gutowski, "SICOR provides a way to prime the surface of these plastics without resorting to hazardous chlorinated solvents or chlorinated primer ingredients."

Because of their molecular structure, polyolefins are exceptionally nonreactive. A look at the structure of the molecule shows that chemically inert hydrocarbon atoms take up all of the available bonding sites. According to current adhesion theories, the main mechanism for adhesion involves intimate molecular contact, attained by intermolecular or valence forces exerted by molecules in the surface layers of the adhesive and adherend. The task then is to create new bonding sites on the surface of the polymer.

In the SICOR process, the untreated substrate is first oxidized using either a flame process or a coronal discharge (electrical arc comprising ionized air) process. Says Gutowski, "When you oxidize the surface you actually convert some elements of the plastic into chemically receptive sites, such as hydroxyl [OH] or carboxyl [COOH] groups. These sites are good for some less demanding bonding-type or printing applications, but not all, and that's where our special chemical treatment comes in."

In the SICOR process, once the surface is oxidized, the next step is to coat it with a graft chemical—a hydrolyzed silane—which provides a molecular "bridge" between the oxidized polymer surface and the material bonded to that surface. The exact nature of the bond between the polymer surface and the silane will vary depending upon the formulation of the silane. At the initial stages of development, the plastic was immersed in the silane solution for a period of up to 30 seconds, then oven-dried, but that step was later replaced by a more industrially practical on-line spray process, followed by a quick drying by an infrared drying element or hot air gun placed above the conveyor.

Gutowski says, "The trick is that one functional end of the graft chemical is reactive with appropriate attachment sites of the oxidized polymer surface, while the other functional group on the same graft chemical is chemically reactive with the material to be put in contact with the SICOR-treated surface. That could be live cells or proteins, adhesive, metallic coating, or any other material of interest to the end user."

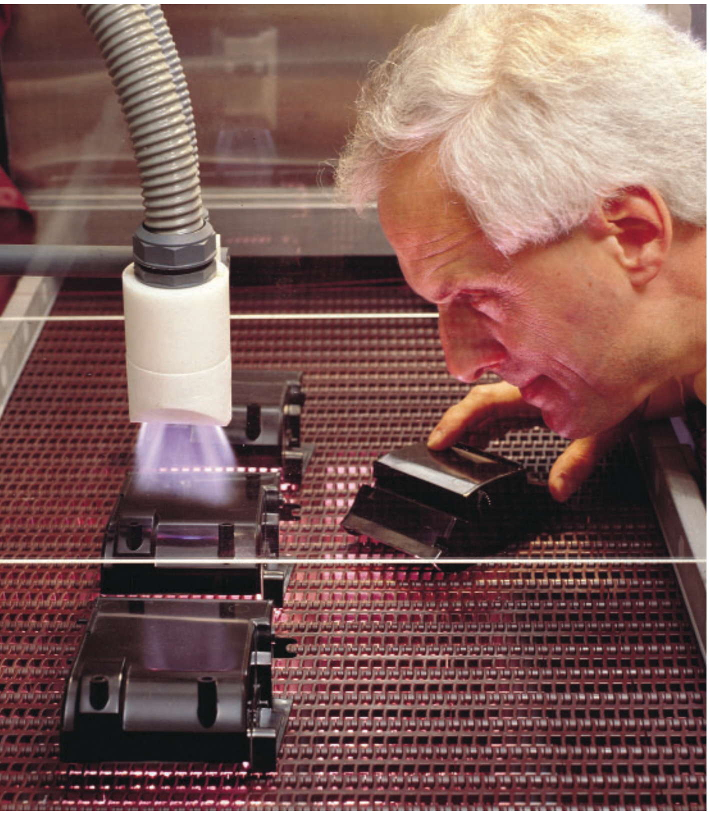
What's left at this point is something that Gutowski describes as "chemical Velcro." The polymer surface has been linked to one end of the applied bonds, while the other end of these molecular bridges waits to latch on to whatever is applied to it: paints, inks, sealants, glues, etc. The SICOR process affects only a molecular layer on the polymer's surface, so the basic properties of the polymer remain unchanged. And once modified, the polymer appears to maintain its newfound abilities indefinitely (samples under study are at two years and counting).

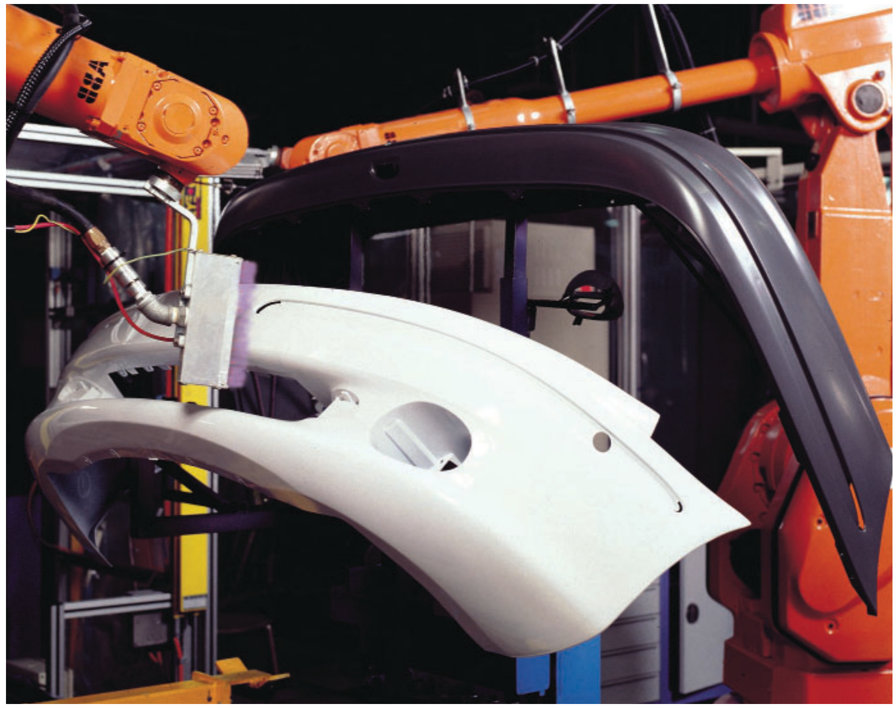
Opher Yom-Tov, a former General Motors design/project engineer, says the benefits of the SICOR process are twofold: it will reduce or eliminate the need for toxic chemicals in plastic processing for the industry, and it will allow for the use of more lightweight plastics components. "Before this process was developed," he says, "most components, like side moldings, were made of extruded PVC [polyvinyl chloride]. PVC is quite a hazardous substance to manufacture, as it requires a great many additives to make it moldable, and gives off many noxious chemicals, including chlorides, which can combine with water vapor to form hydrochloric acid. PVC is also under heavy fire as a source of dioxin. Polypropylene is inexpensive, and it's easy and pretty safe to manufacture."

Revving Up

While the SICOR process is still being developed for use in the automotive painting process, many engineers are already enthusiastic over this process that calls for fewer solvents, increases adhesion, and facilitates the recycling of automotive parts—something being increasingly emphasized as countries around the world struggle to reduce the mass crowding of shrinking landfill areas.

Auto manufacturers may use polypropylene in body side protective moldings and





Building better bumpers. (left) Voytek Gutowski, developer of the SICOR process, examines a prototype corona treatment production line. (right) The SICOR process will soon be marketed for worldwide automotive applications including use in body side protective moldings and bumper bars.

bumper bars, among other applications. CSIRO has run a range of adhesive bonding tests on the SICOR process with good results. For example, using SICOR on low-density polypropylene with a cyanoacrylate created a bond four times stronger than that created by corona discharge alone, while tests of Acetal (the common name for a difficult-to-bond polymer) using two types of silicone sealants showed a strength rating of up to 24 newtons (the unit of force required to detach a 0.5 mm layer of a silicone sealant from the surface of a 1 cm width of SICOR-modified Acetal substrate). By comparison, corona discharge alone yielded a strength rating of 3.25–7.5 newtons.

According to Joseph Gomory, lead engineer for exterior systems at Holden, his company had traditionally used extruded PVC parts for body side moldings, but, he says, "For our [completely redesigned] VT Series II [car] model, injection molding was required because of the shape of the parts." Injection molding evolved from metal die casting, but unlike molten metals, polymer melts have a high viscosity and cannot simply be poured into a mold. Instead, a large force must be used to inject the polymer into a hollow mold cavity. Injection molding is the most widely used process for making parts, as part complexity is virtually unlimited, sizes can range from small to very large, and excellent tolerance control is possible. Disadvantages include high initial equipment investment, high startup and run costs, and the fact that the part itself must be designed for effective molding. During the development phase of the VT Series II program, says Gomory, the company encountered "serious injection molding problems with the PVC body side moldings being developed by our supplier. . . . Our engineers were aware of the SICOR process, which had been experimentally evaluated for adhesion, and judged it to be suitable for production. We decided to implement the SICOR process using polypropylene to achieve a significant cost and mass reduction over PVC."

Gomory explains that the weight of body side moldings is dependent on their shape, but is generally around 1.0–1.5 kg on most Holden vehicles. Because the specific gravity of PVC is around 1.4 while that of polypropylene is around 0.9, a weight savings of approximately 0.5 kg was achieved by using SICOR. "This is a small amount compared to the 1,500 kg mass of typical vehicles," he says, "but is quite significant when it comes to typical mass reduction efforts in the car industry."

Holden entered into a joint development program with CSIRO, plastic injection molding and tooling company Socobell, and ADX, a New Zealand machinery supplier, to set up production facilities for SICOR, where polypropylene would be prepared for both adhesion and painting. "All requirements for adhesion were met [in the testing]," says Gomory, "but we ran into some difficulties with painting. The surface activation energy required from the flaming process for preparation of surfaces prior to the application of the SICOR fluid for a part that is to be painted is higher than that for a surface being prepared for adhesion. Unfortunately for us, the painted version of the body side moldings was deleted from the program for other reasons before we had a chance to resolve these problems."

Says Gomory, "Initially, I think CSIRO underestimated the robustness requirements needed for the SICOR process in an industrial environment, especially for painting. The shape of parts is limited by standard commercially available flaming units, as the correct flame zone has to contact all relevant surfaces of the part to be treated. This can be overcome by designing special flame units to suit the part, but this would be expensive." He continues, "In industry, we also have human error, process variability, wear and tear on equipment, contamination, and a whole host of things that can go wrong. Sufficient safety margin is required in an industrial process to allow for these things, and the SICOR fluid needed to be robustly formulated to cater to these variables. Additionally, the design and construction of the SICOR machine is very important."

Nonetheless, the SICOR process opens some intriguing new avenues, as it will allow

CSIRO Building, Construction, and Engineering for the possible use of lighter-weight and more easily recyclable plastics, processes that use fewer environmentally unfriendly chemicals, and both plastics and processes that are less expensive. CSIRO is continuing its development of the SICOR process to meet the more stringent requirements for painting of parts in an industrial environment. "We hope to evaluate these developments in the near future," Gomory says, "and we may then use the SICOR process for painted parts."

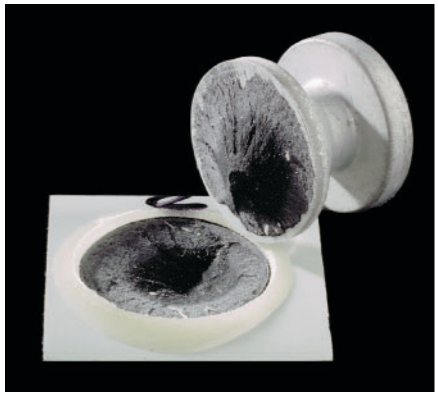
Costs and Benefits

The SICOR process costs an estimated 8–10 times less to use than the plasma technology currently in use for painting and adhesion, and it's a continuous-flow process, capable of being used at conveyor speeds up to 300 m/min, so it can be easily incorporated into an existing process line (unlike plasma, which is a batch process operation). The SICOR unit itself costs less than $500,000, compared to the $2.5 million of a plasma treatment unit, and cost estimates for 5,000-unit auto bumper bar treatment runs about 3¢ per unit for SICOR, compared to about 23¢ per unit for plasma treatment.

Current automobile manufacturing relies heavily on a variety of plastics to reduce weight and improve mileage, while enhancing safety. One problem for the industry, according to Gutowski, is that plastic units are frequently composed of several different plastics: an instrument panel, for example, might include an ABS polycarbonate substrate so that it won't shatter in an accident, covered by a PVC or polyethylene foam for a soft touch and topped off by colored vinyl.

"These materials can't be processed together for recycling," Gutowski says, "because the resulting mix won't have any of the [original] desired properties. It's like mixing water and oil, or one of those marble cake mixes, where the layers remain distinct from one another, yielding no mechanical integrity. On the other hand, the new generation all-polyolefins instrument panels comprising polyethylene foam and polypropylene [parts] can be processed together, which would make the whole recycling process much more economical."

Mark Sofman, manager of industry affairs for the Vinyl Institute of Arlington, Virginia, says, "When you look at cars from the recycling side, probably 75% of the car gets recycled, but that's mostly the metallic components, because it's easy to separate out iron and steel using magnets and eddy currents to remove the aluminum. Because of the number of different types of plastics used in a car, recycling auto plastics is a tremendous challenge."



A sticky situation. SICOR is a new-generation bonding technology that enables the sticking together of previously unbondable or hard-to-bond materials.

Most polypropylene currently taken from scrapped vehicles comes from battery casings, Sofman says. "U.S. law requires the dismantler to remove them because of the lead and sulfuric acid. And plastic fuel tanks, which are also removed because of the risk of explosion, are made from polyethylene. The challenge for industry is how to separate out the great variety of plastics."

SICOR might not have an immediate impact on recycling, says Sofman, but rather an incremental one. Everything is driven by economics, he says, and the approach that provides the best return on investment will be the one that goes furthest. "A good manufacturer is always looking for the next good process," he opines. "To the extent that a new surface treatment technology allows them to get there, people will pay for such a process."

Gutowski envisions SICOR being used across a broad range of possibilities, including medical apparatuses, construction and architectural materials, and the broadening of the range of useful substrates to include materials not used until now because of adherence problems, such as polyvinylidene fluoride (useful because of its resistance to acids, aliphatic and aromatic hydrocarbons, combustion, and aging).

In fact, CSIRO recently signed a $16 million licensing agreement with an undisclosed U.S. building products company to support a new line of building products using recycled polyethylene, and Venture Industries, one of the largest producers of motor vehicle components in the United States, is working with CSIRO to develop a fully commercial version of SICOR.

Before SICOR becomes widely used, a few issues will have to be dealt with. "The process seems to be very sensitive to the machinery used," says Yom-Tov. "It's important that such a process have good [quality control] in its setup and design. With SICOR, you need to be sure of just the right flame temperature and just the right speed of parts through the machine. It seems to be a stable process, once you get it up and running, but there was a lot of trial and error for us to get it just right. It's going to be an educational process, as each user builds on the experiences of the previous users. I think there's a good deal of research and development still ahead to understand the full impact of this technology, and there's just not enough data in yet to remove all of the risks."

It's a new process, Gutowski agrees, and he adds that the people that are potential users need to be convinced that it's a reliable technology before they move away from older tried-and-true methods.

"We'll have to continue to demonstrate its robustness and cost-effectiveness in a variety of industries, and its benefits to the environment and to the health of the workers in those industries," he says. "But I think, once fully verified, the range of applications is such that only our imaginations will provide the limitations."

Lance Frazer

Suggested Reading

Gutowski WS, Pankevicius ER. A novel surface treatment process for enhanced adhesion of ultra-high modulus polyethylene to epoxy resins. Composite Interfaces 1(2):141–151 (1993).

Gutowski WS, Russell L, Hoobin P, Filippou C, Li S, Bilyk A. A novel technology for enhanced adhesion of paints and adhesives to automotive TPOs. In: Proceedings of TPOs in Automotive 2000, 23–25 October 2000, Novi, Michigan. Plymouth, Michigan: Executive Conference Management, Inc., 2000.

Gutowski WS, Wu DY, Li S. Process improvements for treatment of TPOs for enhanced adhesion of paints, sealants and adhesives. In: Proceedings of the 1999 Society of Plastics Engineers Automotive TPO Global Conference, Dearborn, Michigan. Troy, Michigan: Society of Plastics Engineers, 1999.

Gutowski WS, Wu DY, Li S. Surface silanization of polyethylene for enhanced adhesion. Journal of Adhesion 43:139–155 (1993).

CSIRO Building, Construction, and Engineering